

THE EFFECT OF MONO- AND DISUBSTITUTION  
OF THE PHENOLIC RING WITH TERTIARY BUTYL-,  
1-PHENYLETHYL AND CYCLOHEXYL GROUPS  
ON THE ANTIOXIDATIVE ACTIVITY IN THE INITIATED OXIDATION  
OF TETRALIN

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The effect of substitution of the phenolic ring with tertiary butyl, 1-phenylethyl or cyclohexyl groups on the antioxidative activity in the initiated oxidation of tetralin at 60°C was investigated. The substituents in the phenols under investigation were in positions 2-, 4-, 2, 4- and 2,6-; 28 compounds were investigated. The effect of substitution was evaluated by using oxygen consumption. The unfavourable effect of the presence of the 1-phenylethyl group in the ortho position with respect to the hydroxyl group was demonstrated.

Quite a considerable number of papers has been devoted to the investigation of the effects of substituents on the antioxidative properties of alkylated mononuclear phenols (*e.g.*<sup>1-7</sup>). The investigations were carried out in various substrates and by using various experimental techniques and methods of evaluation. This makes a detailed evaluation of effects of the individual aspects of substitution of the phenolic ring more difficult. We tried to render the knowledge of the effects of alkylation more accurate and uniform<sup>7</sup> by a systematic study of the inhibitive properties of a large number of mononuclear phenols in the oxidation of tetralin and isotactic polypropylene. This was part of a rather extensive investigation having as its aim the determination of basic effects of substituents appearing in one-component stabilizing systems for hydrocarbon low-molecular weight and polymeric substrates. In the literature there exists a single one, and only indicative, information about the effect of substitution with aralkyl groups<sup>8</sup>, although some phenols thus substituted have been suggested as effective technical stabilizers.

Here we report results obtained by an extensive study of the effect of substitution of phenols with the 1-phenylethyl group, either alone or combined with the tert-butyl or cyclohexyl group, on the antioxidative activity in the initiated oxidation of tetralin<sup>9</sup>.

## EXPERIMENTAL

*Substrate and antioxidants.* Tetralin (BDH-Chemical Ltd.) was purified before the oxidation according to ref.<sup>13</sup> and redistilled in an inert atmosphere at 206°C. Model antioxidants of type *I* and *II* were obtained by alkylating phenol with isobutylene, cyclohexene or styrene, treating the mixtures by column chromatography and repeated purification<sup>9</sup>. The purity was determined by thin-layer and gas chromatography. The characteristics of compounds *IIIi–IIIj*, *IIIr*, *IIIt–IIIv* so far undescribed are given in Table I. The characteristics of the other known model compounds agreed with the literary data. The IR spectra were recorded<sup>10</sup> with a UR-20 (C. Zeiss, Jena) apparatus at 25°C (cell 16 mm, CCl<sub>4</sub>) and 110°C (thermostated cell 10 mm, CHCl<sub>2</sub>CHCl<sub>2</sub>) in the range of 3400–3800 cm<sup>-1</sup> at a concentration 10<sup>-2</sup> mol/l.

*Determination of antioxidative activity.* The antioxidative activity of phenols of type *I* and *II* was examined by measuring oxygen absorption in tetralin oxidized in an apparatus with automatic recording<sup>11</sup> at 60 ± 0.1° in pure oxygen with 2,2'-azobis (isobutyronitrile) as initiator. The concentration of the antioxidants was 1 · 10<sup>-3</sup> mol/l, that of the initiator was 2.8 · 10<sup>-2</sup> mol/l. From the absorption curves thus obtained, τ<sub>100</sub> and τ<sub>200</sub> were read off as times needed for the

TABLE I  
Characteristics of New Phenols of Type *II*

Compound	Mol. formula (mol. weight)	B.p., °C/Pa	Calculated/Found	
			% C	% H
<i>IIIi</i>	C <sub>16</sub> H <sub>24</sub> O (232.3)	110–1/93.32	82.70	10.41
			82.66	10.29
<i>IIIj</i>	C <sub>18</sub> H <sub>22</sub> O (254.3)	121–3/10.66	84.99	8.72
			84.87	8.59
<i>IIIk</i>	C <sub>20</sub> H <sub>24</sub> O (280.4)	83/33.33	85.66	8.62
			85.52	8.48
<i>III</i>	C <sub>16</sub> H <sub>24</sub> O (232.3)	99–100/93.32	82.70	10.41
			82.44	10.12
<i>III</i> <i>m</i>	C <sub>20</sub> H <sub>24</sub> O (280.4)	143–5/33.33	85.66	8.62
			85.39	8.50
<i>III</i> <i>r</i>	C <sub>13</sub> H <sub>18</sub> O (190.3)	112–3/39.99	82.05	9.53
			81.98	9.44
<i>III</i> <i>t</i>	C <sub>14</sub> H <sub>14</sub> O (198.3)	124–6/53.32	84.81	7.11
			84.77	7.03
<i>III</i> <i>u</i>	C <sub>15</sub> H <sub>16</sub> O (212.3)	127–8/2.66	84.86	7.59
			84.82	7.64
<i>III</i> <i>v</i>	C <sub>16</sub> H <sub>18</sub> O (226.3)	118/39.99	84.91	8.01
			84.77	7.90

absorption of 100 and 200 ml of oxygen per 1 ml of tetralin. 2,6-Di-tertbutyl-4-methylphenol was used as standard. The relative activities  $A_{rel}$  were calculated by using the relationship<sup>12,13</sup>  $A_{rel} = (\tau' - \tau)/(\tau^0 - \tau)$ , where  $\tau'$  is the value of  $\tau_{100}$  in the presence of the antioxidant under investigation,  $\tau$  is the value for unstabilized tetralin,  $\tau^0$  is the value obtained in the presence of the standard. A similar procedure was used for calculating<sup>13</sup> the slopes  $S = 100/(\tau_{200} - \tau_{100})$  for the intercept of the absorption curve at a stabilized rate of oxidation after completion of the induction period;  $S_{rel} = S'/S$ , giving the ratio of slopes for tetralin containing the antioxidant ( $S'$ ) and without the latter ( $S$ ). The absorption curves were used for the graphic determination of the induction periods  $\tau_0$  (s), which were employed in calculating the stoichiometric factor  $n$  according to the relationship<sup>13,14</sup>  $n = 2e(c_i - c_i e^{-k_i t_0})/c_a$ , where  $e$  is the activity factor of the initiator (0.6),  $k_i$  is the rate constant of decomposition of the initiator ( $1.0 \cdot 10^{-5} \text{ s}^{-1}$ ),  $c_i$  and  $c_a$  are the initial concentrations of the initiator and antioxidant (mol/l).

## RESULTS AND DISCUSSION

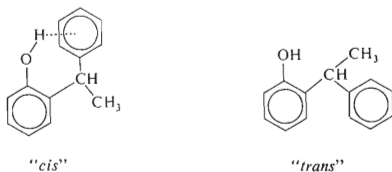
The compounds chosen for the investigation were phenol (*Ia*), 2-alkylphenols (*Ib–Id*), 4-alkylphenols (*IIa–IId*), 2,4-dialkylphenols (*IIe–IIv*) and 2,6-dialkylphenols (*Ie–Ig*). We concentrated our attention on phenols substituted with the tertiary butyl, 1-phenylethyl or cyclohexyl group. Some derivatives of *p*-cresol (*IIn–IIv*) containing the same substituents were also used. The antioxidative activity of a one-component antioxidative system was measured at 60°C, when the volatility

TABLE II  
Antioxidative Properties of Phenols of Type *I* and *II* in the Oxidation of Tetralin at 60°C  
Concentration of phenols  $1 \cdot 10^{-3} \text{ mol l}^{-1}$ , of initiator  $2.8 \cdot 10^{-2} \text{ mol l}^{-1}$ ; meaning of symbols  $A_{rel}$ ,  $S_{rel}$  and  $n$  cf. Experimental.

Compound	$A_{rel}$	$S_{rel}$	$n$	Compound	$A_{rel}$	$S_{rel}$	$n$
<i>Ia</i>	0.17	0.44	0.47	<i>IIIh</i>	0.99	0.25	2.79
<i>Ib</i>	0.76	0.31	2.14	<i>IIIi</i>	1.23	0.43	3.44
<i>Ic</i>	0.57	0.31	1.60	<i>IIIj</i>	1.18	0.22	3.32
<i>Id</i>	0.66	0.32	1.86	<i>IIIk</i>	1.10	0.25	3.10
<i>Ie</i>	1.18	0.25	3.32	<i>IIIl</i>	1.23	0.52	3.46
<i>If</i>	0.71	0.39	2.00	<i>IIIm</i>	0.90	0.26	2.53
<i>Ig</i>	0.50	0.76	1.41	<i>IIIn</i>	0.89	0.57	2.50
<i>IIa</i>	0.50	0.26	1.41	<i>IIIo</i>	0.85	0.55	2.39
<i>IIb</i>	0.46	0.41	1.29	<i>IIIp</i>	1.15	0.76	3.24
<i>IIc</i>	0.53	0.30	1.49	<i>IIIr</i>	1.04	0.64	2.93
<i>IId</i>	0.39	0.32	1.09	<i>IIIs</i>	1.18	0.57	3.32
<i>IIe</i>	1.24	0.32	3.49	<i>IIIt</i>	0.96	0.70	2.70
<i>IIf</i>	0.85	0.42	2.39	<i>IIIu</i>	0.90	0.55	2.53
<i>IIg</i>	1.22	0.26	3.44	<i>IIIv</i>	0.61	0.35	1.72

of the antioxidants is not yet operative. The rate of oxidation of tetralin is sufficient under these conditions and allows the effects of substitution on the antioxidative activity to be examined. The rate of oxidation was expressed by using relative activities  $A_{rel}$  (with 2,6-ditert-butyl-4-methylphenol as standard). Hence, the ratios of the slopes  $S_{rel}$  of the straight intercepts of the absorption curves and the stoichiometric factor  $n$  were calculated. The results are summarized in Table II.

One can see some characteristic consequences of substitution. The inhibitive activity due to the *ortho* substitution increases; the presence of the tertiary butyl group (compound *Ib*) and of the cyclohexyl group (compound *Ic*) has a more pronounced effect on  $A_{rel}$  than the 1-phenylethyl group (compound *Ic*). In other words, the specific effect of a bulky *ortho* substituent has been demonstrated. (Other authors found<sup>15,16</sup> in the hydrocarbon substrates a still more pronounced effect due to substitution with the tertiary butyl group in the *ortho* position). At the same time, however, the effect of an interaction of the substituent with the phenolic hydroxyl group also becomes operative. Of the triad of the *ortho* substituents investigated in this work, the antioxidative activity was least influenced by the 1-phenylethyl group. This is a consequence of a different effect upon the course of the primary step in interrupting the kinetic autoxidation chain. In the interaction of the ROO· or RO· radicals with the phenol thus substituted, the tearing-off of the hydroxyl hydrogen atom is more difficult because of the OH... $\pi$  bond. Such an intramolecular bond was proved by recording<sup>10</sup> the IR spectra. It is remarkable that it did not disappear even in measurements carried out at 110°C. Fig. 1 shows the IR spectra of the individual phenols containing the 1-phenylethyl group recorded at 25 and 110°C. The hydroxyl groups in phenols containing in the *ortho* position the 1-phenylethyl group have bands corresponding to the bonded and free OH groups:  $\nu_{OH... \pi} = 3556 \text{ cm}^{-1}$ ,  $\nu_{OH} = 3620 \text{ cm}^{-1}$ . They belong to conformers which can be denoted as being "cis" and "trans" depending on the position of the phenyl group with respect to the hydroxyl group.



For 2-(1-phenylethyl)phenol and 2,4-bis(1-phenylethyl)phenol the ratio of vibrations of the bonded and free hydroxyl group was approximately 63 : 37, for 2,6-bis and 2,4,6-tris(1-phenylethyl)phenol this ratio was approximately 84 : 16.

*p*-Substituted derivatives of phenols *I Ia*–*I Ic* do not virtually exhibit any difference in the contributions of the three substituents under investigation. The relative

activity  $A_{rel}$  calculated from the measured values is low, similarly to  $n$ . On the other hand, the absorption of oxygen on completion of the induction period as demonstrated by the  $S_{rel}$  values is essentially the same as for *o*-monosubstituted derivatives and lies within the range of values which hold for the whole group investigated in this work. This characterizes an analogous effect on the process due to the reaction products arising by the transformation of the individual phenolic antioxidants of the whole group. We did not investigate the nature of the compounds formed in the reaction; they are yellowish, however, which indicates the presence of quinoid or quinomethide structures, for which a retardative effect has been proved in another independent study<sup>17</sup>.

Phenols with unoccupied *ortho* positions towards the hydroxyl group have no possibility of influencing selectively by the steric effect of the substituents the interaction between the  $ROO\cdot$  or  $RO\cdot$  radicals, on the one hand, and the phenolic hydroxyl

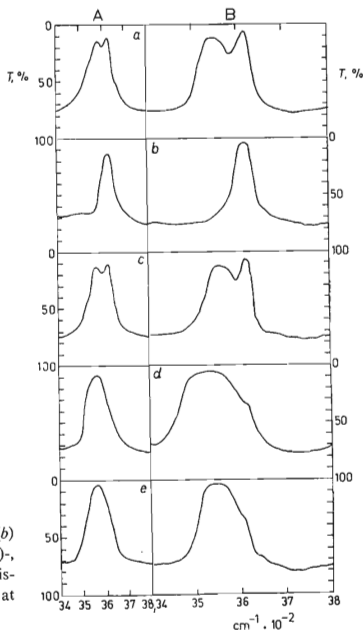


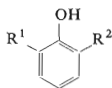
FIG. 1

IR Spectra of (a) 2-(1-Phenylethyl)-, (b) 4-(1-Phenylethyl)-, (c) 2,4-Bis(1-phenylethyl)-, (d) 2,6-Bis(1-phenylethyl)- and (e) 2,4,6-Tris(1-phenylethyl)phenols Measured in  $CCl_4$  at  $25^\circ C$  (A) and in  $CHCl_2CHCl_2$  at  $110^\circ$  (B)

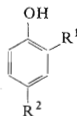
group, on the other, thus contributing specifically to a relative stabilization of the forming aryloxy group. In addition, *para*-monosubstituted phenols are also more readily oxidized directly with oxygen; the process is a competitive one with respect to the interaction with  $\text{ROO}\cdot$ , particularly at elevated temperatures<sup>18</sup>. Therefore from the standpoint of the inhibition process, if one-component stabilizing systems are used, one should prefer antioxidants containing a bulky substituent *ortho*.

Higher antioxidative activities were determined for 2,4-disubstituted phenols containing the same or mixed substituents. 2,4-Di-*tert*-butylphenol (*Iie*) and 2,4-dicyclohexylphenol (*Iig*) exhibited high relative activities  $A_{\text{rel}}$  and the respective high  $n$  values. Unlike this, substitution of the phenolic ring with a second phenylethyl group (compound *Iif*) caused only a small increase in activity compared with monosubstitution of positions 2- or 4-. One may assume that the sum of the polar and steric effects under consideration, which appear in the substitution of *Iie* and *Iig* with the *tert*-butyl and cyclohexyl groups, influences in the optimal way the reaction of phenol with  $\text{ROO}\cdot$  both on the phenolic hydroxy group and in further stages in the unsubstituted *ortho* position, or by geminal interaction in one of the substituted positions. The resulting measured  $A_{\text{rel}}$  values of 2,4-disubstituted phenols *Iie*, *Iig* investigated here (which contain the same substituents) under experimental conditions used correspond to the sum of values measured for 2- and 4-monosubstituted phenols (the difference between the measured  $A_{\text{rel}}$  (2,4-disubstit.) and calculated  $A_{\text{rel}}$  (2-substit. + 4-substit.) is 0.02 for 2,4-ditertbutylphenol and 0.03 for 2,4-dicyclohexylphenol). For 2,4-bis(1-phenylethyl)phenol (*Iif*) the difference between the calculated and measured values is larger (0.18).

A rather small contribution of the phenylethyl group to the total activity can also be observed with 2,4-disubstituted phenols, where the phenylethyl group is combined with another substituent.  $A_{\text{rel}}$  of all compounds in which 1-phenylethyl group is in the *ortho* position and position 4 has been substituted with the methyl group (compound *Iiu*), tertiary butyl group (compound *Iih*), or cyclohexyl group (compound *Iim*),  $A_{\text{rel}}$  is lower than unity (varying between 0.90–0.99). Here again there is a negative effect of the intramolecular hydrogen bond  $\text{OH}\dots\pi$  on the inhibition process. If the phenylethyl group is in position 4, then by substituting position 2 with the tertiary butyl (compound *Iij*) or cyclohexyl (compound *Iik*) groups one may attain activity always exceeding the standard one. In no case, however, is it possible to reach  $A_{\text{rel}}$  characterizing the activity of 2,4-disubstituted phenyls containing the tertiary butyl or cyclohexyl groups, both in the homogeneous (compounds *Iie* and *Iig*) and in the nonhomogeneous (compounds *Iii*, *Iil*) disubstitution. Also in this group of disubstituted phenols the specifically less advantageous effect of the aralkyl group has been proved compared with the tertiary alkyl and cycloalkyl group; the way in which the position *ortho* towards the hydroxyl group has been substituted is particularly important. The substitution of the *para* position with the aralkyl group under investigation already has a lower negative effect.



- Ia*,  $R^1 = R^2 = H$   
*Ib*,  $R^1 = t-C_4H_9$ ,  $R^2 = H$   
*Ic*,  $R^1 = CH_3(C_6H_5)CH-$ ,  $R^2 = H$   
*Id*,  $R^1 = C_6H_{11}$ ,  $R^2 = H$   
*Ie*,  $R^1 = R^2 = t-C_4H_9$   
*If*,  $R^1 = R^2 = CH_3(C_6H_5)CH-$   
*Ig*,  $R^1 = R^2 = C_6H_{11}$



- IIa*,  $R^1 = H$ ,  $R^2 = t-C_4H_9$   
*IIb*,  $R^1 = H$ ,  $R^2 = CH_3(C_6H_5)CH-$   
*IIc*,  $R^1 = H$ ,  $R^2 = C_6H_{11}$   
*IId*,  $R^1 = H$ ,  $R^2 = CH_3$   
*IIe*,  $R^1 = R^2 = t-C_4H_9$   
*IIf*,  $R^1 = R^2 = CH_3(C_6H_5)CH-$   
*IIg*,  $R^1 = R^2 = C_6H_{11}$   
*IIh*,  $R^1 = CH_3(C_6H_5)CH-$ ,  $R^2 = t-C_4H_9$   
*IIi*,  $R^1 = C_6H_{11}$ ,  $R^2 = C_4H_9$   
*IIj*,  $R^1 = t-C_4H_9$ ,  $R^2 = CH_3(C_6H_5)CH-$

- IIk*,  $R^1 = C_6H_{11}$ ,  $R^2 = CH_3(C_6H_5)CH-$   
*III*,  $R^1 = t-C_4H_9$ ,  $R^2 = C_6H_{11}$   
*IIIm*,  $R^1 = CH_3(C_6H_5)CH-$ ,  $R^2 = C_6H_{11}$   
*IIIn*,  $R^1 = R^2 = CH_3$   
*IIo*,  $R^1 = C_2H_5$ ,  $R^2 = CH_3$   
*IIp*,  $R^1 = t-C_4H_9$ ,  $R^2 = CH_3$   
*IIr*,  $R^1 = C_6H_{11}$ ,  $R^2 = CH_3$   
*IIs*,  $R^1 = l-CH_3-C_6H_{10}$ ,  $R^2 = CH_3$   
*III*,  $R^1 = C_6H_5-CH_2-$ ,  $R^2 = CH_3$   
*IIU*,  $R^1 = CH_3(C_6H_5)CH-$ ,  $R^2 = CH_3$

For the sake of comparison we examined the effect of the character of the *ortho* substitution also in a supplementing series of 2-substituted 4-methylphenols *IIIn-IIIv*. One should mention the relatively higher values of  $S_{rel}$  of almost all antioxidants in this group and the high values of the stoichiometric coefficient of the most active compounds *IIp-IIIs*. All possess a bulky aliphatic substituent in the *ortho*-position. In this group too the *ortho*-aralkyl group is little advantageous. A comparison of *III-IIIv* also reveals the negative effect of branching of the aralkyl substituent on the  $\alpha$ -carbon atom, indicated also by measurements carried out on another substrate<sup>8</sup>. The negative effect increases in the series benzyl <  $\alpha$ -methylbenzyl <  $\alpha,\alpha$ -dimethylbenzyl. This is probably due, above all, to a decrease in the reactivity with the alkylperoxy groups.

The last group of compounds investigated in this work were 2,6-disubstituted phenols *Ie-Ig*. All of them are less active compared with similarly 2,4-disubstituted isomers. The relative activity of 2,6-bis(1-phenylethyl)phenol (*If*) is particularly low. Its IR spectrum (Fig. 1) indicates a high content of intramolecular hydrogen bonds  $OH \cdots \pi$ , which can be regarded as an explanation of the reduced reactivity with the  $ROO\cdot$  radicals.

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## REFERENCES

1. Wasson J. I., Smith W. M.: *Ind. Eng. Chem.* **45**, 197 (1953).
2. Ingold K. U.: *J. Phys. Chem.* **64**, 1636 (1960).
3. Bickel A. F., Kooyman E. C.: *J. Chem. Soc.* **1960**, 2215.
4. Scott G.: *Chem. Ind. (London)* **1963**, 271.
5. Hedenburg J. F.: *Ind. Eng. Chem. Fundam.* **2**, 265 (1963).
6. Low H.: *Ind. Eng. Chem. Prod. Res. Develop.* **5**, 80 (1966).
7. Prusíková M., Kotulák L., Pospíšil J.: *39th International Congress of Industrial Chemistry, Bucuresti 1970, Proceedings Vol. 4*, p. 247.
8. Spacht R. B., Wedelin C. W., Hollinghead W. S., Wills D. C.: *Ind. Eng. Chem. Prod. Res. Develop.* **1**, 202 (1962).
9. Holčík J.: *Thesis*. Slovak Academy of Sciences, Bratislava 1974.
10. Hrdlovič P., Schubertová N.: Unpublished results.
11. Kotulák L., Švantner J., Pospíšil J.: *Chem. Listy* **68**, 78 (1974).
12. Rosenwald R. H., Chenicek J. A.: *J. Amer. Oil Chem. Soc.* **28**, 185 (1951).
13. Prusíková M., Jiráčková L., Pospíšil J.: *This Journal* **37**, 3788 (1972).
14. Zikmund L., Taimr L., Čoupek J., Pospíšil J.: *Eur. Polym. J.* **8**, 83 (1972).
15. Bickoff E. M., Livingston A. L., Thompson C. R.: *J. Amer. Oil Chem. Soc.* **29**, 445 (1952).
16. Davies D. S., Goldsmith H. L., Gupta A. K., Lester G. R.: *J. Chem. Soc.* **1956**, 4926.
17. Buben I., Pospíšil J.: *This Journal* **40**, 977 (1975).
18. Lerchová J., Pospíšil J.: *J. Polym. Sci. C* **40**, 307 (1973).

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